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Flora Tak Tak NG et al.  
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**AMENDMENTS UNDER PCT ARTICLE 34  
(ARTICLE 34 AMENDMENTS)**

**International Application No.: PCT/CA2004/002111**

**MAIL STOP - PCT**

**Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450**

Sir:

**REQUEST FOR SUBSTITUTION OF REPLACEMENT SHEETS**

Please substitute the attached replacement sheets 1, 1a, 3, 5, 6, 6a, 8, 8a, 15, 15a, 16, 16a, and 54-60, containing the Article 34 Amendments filed June 6, 2005, for sheets 1, 3, 5, 6, 8, 15, 16, and 54-61, of the enclosed as-filed PCT application. It is respectfully requested that the claims contained in replacement sheets 54-60, be examined during examination of the patent application. Claims 1-49 are currently pending.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,  
GARRETT & DUNNER, L.L.P.

Dated: June 9, 2006

By: 

Ernest F. Chapman  
Reg. No. 25,961

EFC/FPD/blc

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**AMENDED SHEETS ATTACHED TO AMENDMENT UNDER  
ARTICLE 34 OF THE PCT, DATED JUNE 6, 2005**

COMPOSITE CATALYST FOR THE SELECTIVE OLIGOMERIZATION OF  
LOWER ALKENES AND THE PRODUCTION OF HIGH OCTANE PRODUCTS

FIELD OF THE INVENTION

This invention relates to the oligomerization of lower  
5 alkenes and mixtures of alkenes by catalytic distillation.  
More specifically, the invention relates to a catalytic  
composite as a catalyst and packing media in a catalytic  
distillation column for the selective oligomerization of  
lower alkenes. In addition, the invention also relates to  
10 the hydrogenation of alkenes or of the products from the  
selective oligomerization to produce high octane products.

BACKGROUND OF THE INVENTION

Catalytic distillation (CD) combines catalytic reaction and  
separation in a single distillation unit. This idea was  
15 first implemented early in the 1920s for the production of  
esters (Backhaus, US Patent No. 1,400,849) and has been  
applied to a number of chemical processes based on  
homogeneous catalysts. The advantages of combining reaction  
and separation were not fully appreciated until 1980, when  
20 Smith patented a new catalytic distillation technology using  
heterogeneous catalysts (Smith, US Patent No. 4,232,177).

Conventional chemical processes that utilise a distillation  
process (non-catalytic) mainly consist of two separate unit  
operations. These include a unit hosting chemical reactions  
25 and another unit for separating the different components  
from the resulting reaction mixture. Under such  
circumstances, it is difficult to recycle the heat produced  
by the chemical reaction, and cooling is often needed to  
control the temperature in the reaction zone, thus resulting  
30 in ineffective energy utilization in the process. In

addition, the productivity of a preferred compound is often

sufficient catalyst is placed into the column without significantly increasing the pressure drop. It was not until 1980 that Smith (US Patent No. 4,232,177) patented a method of suspending catalyst pellets inside a distillation column using fibreglass containment bags, which are known as Texas teabags. Use of these bags permits the use of heterogeneous catalysts without giving rise to large increases in pressure drop. In contrast to homogeneous catalytic distillation, heterogeneous catalytic distillation is preferentially termed catalytic distillation (CD).

In the CD process, the solid catalyst has to be packed in a suitable manner inside the distillation column so as to maximize contact between vapour and liquid phases, but to minimize column flooding. Indeed, various methods have been reported for supporting or containing catalysts [Crossland et al., US Patent 5,431,890; Hearn, US Patent 5,266,546; Shelden, US patent 5,417,938]. It should be noted that with all these methods, the catalyst is enclosed inside a device which can increase the mass transfer resistance of the liquid and gas phases in the column.

Since a catalytic distillation process combines heterogeneous reaction and separation in a single distillation column, the following advantages can often be obtained over conventional fixed bed reactors:

- i) The capital and production costs are reduced because two operations are combined in a single unit.
- ii) The energy consumption can be minimized as the heat of the reaction is used for the in-situ vaporization of the reactants.
- iii) The conversion of the reactant can be enhanced through internal recycling.

ii) The catalyst should be heterogeneous and stable thermally as well as chemically and physically to retain its structural integrity for maintenance of a long lifetime.

iii) The reaction should be exothermic and in situations where the reaction is equilibrium limited, the CD process presented the option to shift that equilibrium more to the right to achieve higher conversion and higher productivity much more efficiently.

One chemical reaction that satisfies these requirements is the oligomerization of lower alkenes (alkene molecules having from 2 to 6 carbon atoms). Alkylation and oligomerization of lower alkenes was first disclosed by Huss and Kennedy (US Patent No. 4,935,577) and Smith et al. (US Patent No. 5,003,124). The oligomerization of lower alkenes is an important industrial reaction and represents a route to the production of intermediates used for the production of motor fuels, plasticizers, pharmaceuticals, dyes, resins, detergents, lubricants and additives (O'Connor and Kojima, 1990). With respect to butene oligomerization, the less branched dimer products, octenes, are particularly useful in the manufacture of plasticizers. If heavily branched, the mixture can be used as a gasoline blender.

Historically, the exploitation of all of the C<sub>4</sub> fractions obtained as by-product from hydrocarbon fluid catalytic cracking and steam cracking to produce high value products (high octane value product) has been lacking. Butadiene, a component of the by-product is useful for rubber production and is extracted from the by-product, leaving the remaining C<sub>4</sub> fractions as a mixture referred to as Raffinate I. The isobutene that is contained in Raffinate I was used as a source for production of methyl tert-butyl ether (MTBE). The remaining components of the C<sub>4</sub> fractions after the removal of

isobutene, consisting mainly of linear C<sub>4</sub> hydrocarbon (butenes), was mainly used as a gasoline blender, albeit a poor one. In certain cases, this product was simply disposed of by flaring. In Raffinate II, n-butene is present at an  
5 average content from 70% to 80% and in some cases can be in the ninety percentage ranges. Using this resource, smaller oligomers, particularly C<sub>8</sub> and C<sub>12</sub>, are being produced by current catalytic oligomerization processes.

A variety of butene oligomerization processes have been  
10 proposed (Keim et al, J. Mol. Catal., 6, 79, 1979; Mathys et al, US Patent No. 4,476,341; and Beltrame et al., Appl. Catal., A: general, 100, 39-48, 1994) based on homogeneous and heterogeneous reactions. These processes are exclusively focused on the catalyst selection and process optimization  
15 so that a high oligomerization rate with a high selectivity to desired products, mainly short and less branched oligomers, can be obtained.

The use of catalytic distillation to enhance the oligomerization of alkenes was first disclosed in US Patent  
20 No. 5,003,124 to Smith in 1991. This process utilized an acidic ion exchange resin placed inside a fibre glass bag.

Further research has been carried out in the field of alkene oligomerization, but in most cases, the oligomerization catalyst is contained within a second structure such as a  
25 cloth or mesh bag, and the reactants have to pass through this structure to access the catalyst. Likewise, the products have to pass through the structure to be removed away from the catalyst. In one such example, Podrebarac ("The Dimerization of 1-Butene Using Catalytic  
30 Distillation", M.A. Sc. Thesis, University of Waterloo, 1992) studied butene dimerization in a CD column using a

nickel exchanged zeolite catalyst, where the zeolite was placed directly in fibreglass bags. The zeolite catalyst in this case was quickly deactivated by the production of undesirable long chain oligomers, which oligomers blocked

hollow cylinder, a cross or multi partition ring or cylinder with 2, 3, or 4 cell partitions, a saddle, a solid ring, a solid cylinder, a sphere, and a honeycomb body; and

b) from 0.01 to 10% by weight of a catalytically active species, based on the weight of the catalyst, which is deposited on the support structure.

In another aspect, the present invention provides a catalytic composite for use as a hydrogenation catalyst in a catalytic distillation apparatus, the catalytic composite comprising:

a) a support structure, made of an inorganic oxide, having a void fraction ranging from 0.30 to 0.95 and a crush strength of from 2.4 to 9.9 kg per structure unit, the support structure having a shape selected from a ring, a hollow cylinder, a cross or multi partition ring or cylinder with 2, 3, or 4 cell partitions, a saddle, a solid ring, a solid cylinder, a sphere, and a honeycomb body; and

b) from 0.01 to 10% by weight of palladium, platinum or rhodium, based on the weight of the catalytic composite, which is deposited on the support structure. In one embodiment, the inorganic oxide forming the support structure of the hydrogenation catalyst is an  $\alpha$ -alumina, for example an  $\alpha$ -alumina having a surface area of from 0.1 to 1.0 m<sup>2</sup>/g.

In still another aspect, the present invention provides a process for the selective oligomerization of a lower alkene to a C<sub>6</sub>-C<sub>18</sub> alkene, which process comprises contacting the lower alkene with a catalytic composite as described herein, under catalytic distillation conditions.

In still another aspect, the present invention provides a process for the hydrogenation of an alkene to an alkane, which process comprises contacting the alkene with a catalytic composite as described herein, and hydrogen, under  
5 catalytic distillation conditions.

properties comprising of both components to constitute or form the catalytic composite.

Various catalytically active species can be deposited on the support structures described above to give the catalytic composite. Examples of active species include metals and metal ions from Groups VI, VII and VIII. These metals or metal ions can be loaded from corresponding metal salts or metal complexes. Of these metals and metal ions, nickel ions loaded from nickel salts, which are especially effective for the oligomerization of lower alkenes, are preferred as the active species for oligomerization. Examples of metal salts include metal sulphate, metal phosphate, metal oxalate and metal acetate. More preferably, the nickel ions loaded from aqueous solutions of nickel sulphate, or aqueous solutions of nickel chloride and ammonium sulphate are used as the active catalytic species. Metals used as the catalytic species for oligomerization are also preferably in the +1 or +2 oxidation state. As the oligomerization is acid catalysed, acid and acidic salts can be deposited on the support and used as catalyst. In addition, the oligomerization catalysts comprising nickel ions can be further enhanced through exposure to solutions of sulphate salts such as ammonium sulphate, phosphate salts such as ammonium phosphate and acids such as sulphuric acid, phosphoric acid or toluenesulfuric acid. Such solutions are herein referred to as catalyst enhancers.

The catalytically active species are not necessarily metallic, as certain salts, such as ammonium sulphate, can be used. For example, ammonium sulphate is a suitable catalytically active species for the dimerization of isobutene in the presence of hydrogen.

Metal loaded from metal complexes of palladium, platinum, rhodium and nickel are effective for hydrogenation of alkenes, including hydrogenation of octenes and methyl

substituted pentenes produced by the oligomerization of butenes by the nickel catalyst described herein. Metal complexes can contain ligands comprising, for example, one or more carbon, hydrogen, oxygen, nitrogen and phosphorus atoms. Metal salts can also be used as catalytic species in the hydrogenation process if the metal ions derived from the salts can be reduced to give metal species that are active.

The amount of catalyst species on the support structure is dependent on the concentration of metal salt or the metal complex in solution, and to a lesser extent on the length of the exposure period of the support structure to the solution. The amount of catalytic species can be from 0.01 to 10% by weight, for example of from 0.05 to 10% or from 0.1 to 8% by weight.

A catalytic composite for use as an oligomerization catalyst can, for example, contain nickel in an amount of from 0.1 to 8% by weight, relative to the weight of the composite. Preferably, the amount of nickel is from 0.2 to 6.0% by weight, and more preferably, from 0.5% to 5% by weight.

A catalytic composite for use as a hydrogenation catalyst can, for example, contain palladium in an amount of from 0.05 to 8% by weight, relative to the weight of the composite. Preferably, the amount of palladium can be, for example, from 0.1 to 8%, from 0.2 to 6%, from 0.2 to 5%, from 0.5 to 5% or from 0.3 to 2% by weight.

Deposition of the metal ions on the support structure can be effected by methods known in the art. Examples of such methods include wet and dry impregnation methods, vaporization methods, absorption techniques, ion-exchange techniques, sol-gel techniques and vapour deposition

techniques. A description of such techniques is given in examples 1a and 1b.

#### *Catalytic Distillation Packing*

We claim:

1. A catalytic composite for use as a random packing material and catalyst in a catalytic distillation apparatus, the catalytic composite comprising:

a) a support structure, made of a non zeolite inorganic oxide, having a void fraction ranging from 0.30 to 0.95 and a surface area of from 40 m<sup>2</sup>/g to 500 m<sup>2</sup>/g, the support structure having a shape selected from a ring, a hollow cylinder, a cross or multi partition ring or cylinder with 2, 3, or 4 cell partitions, a saddle, a solid ring, a solid cylinder, a sphere, and a honeycomb body; and

b) from 0.01 to 10% by weight of a catalytically active species comprising a group VIII metal, based on the weight of the catalytic composite, which is deposited on the support structure.

2. The catalytic composite according to claim 1, wherein the void fraction is from 0.30 to 0.95 and the surface area is from 50 m<sup>2</sup>/g to 500 m<sup>2</sup>/g.

3. The catalytic composite according to claim 1 or 2, wherein the inorganic oxide is selected from the group consisting of alumina, silica, titania, zirconia and mixtures thereof.

4. The catalytic composite according to claim 1 or 2, wherein the inorganic oxide is  $\gamma$ -alumina.

5. The catalytic composite according to claim 1 or 2, wherein the inorganic oxide is  $\alpha$ -alumina.

6. The catalytic composite according to any one of claims 1 to 5, wherein the support structure is in the shape of a Raschig ring.
7. The catalytic composite according to any one of claims 1 to 6, wherein the group VIII metal is nickel.
8. The catalytic composite according to any one of claims 1 to 7, wherein the group VIII metal is in the form of a metal salt or a metal complex.
9. The catalytic composite according to claim 8, wherein the metal salt is in an ionic state.
10. The catalytic composite according to claim 8, wherein the metal salt is a metal sulphate, a metal phosphate, a metal oxalate or a metal acetate.
11. The catalytic composite according to any one of claims 1 to 6, wherein the catalytically active species is nickel sulphate.
12. The catalytic composite according to any one of claims 1 to 6, wherein the catalytically active species is nickel chloride.
13. The catalytic composite according to any one of claims 9 to 12, wherein the catalytically active species is in admixture with ammonium sulphate or ammonium phosphate.
14. The catalytic composite according to any one of claims 1 to 6, wherein the catalytically active species comprises a group VIII metal and a ligand, wherein the ligand comprises one or more atoms selected from the group consisting of carbon, hydrogen, oxygen, nitrogen and phosphorus.

15. The catalytic composite according to claim 14, wherein the group VIII metal is in the zero oxidation state.

16. The catalytic composite according to any one of claims 1 to 6, wherein the group VIII metal is palladium, platinum or rhodium.

17. Use of a catalytic composite as claimed in any one of claims 1 to 16 as a packing material in a catalytic distillation column.

18. Use of a catalytic composite as claimed in any one of claims 1 to 16 as a catalyst in a catalytic distillation column.

19. A process for the selective dimerization of a lower alkene to a C<sub>6</sub>-C<sub>12</sub> alkene, which process comprises contacting the lower alkene with a catalytic composite as claimed in any one of claims 1 to 16, under catalytic distillation conditions.

20. The process according to claim 19, wherein the lower alkene is selected from 1-butene, 2-butene and isobutene, and the C<sub>6</sub>-C<sub>12</sub> alkene is selected from trimethylpentene, n-octene, dimethylhexene and methylheptene.

21. The process according to claim 19 or 20, wherein the catalytic composite is admixed with inert distillation packing.

22. The process according to claim 21, wherein the ratio of the catalytic composite to inert distillation packing is from 10:1 to 1:10.

23. The process according to claim 21, wherein the catalytic composite and inert distillation packing are used in separate zones of the catalytic distillation column.

24. The process according to claim 19, wherein the lower alkene is a C<sub>4</sub> alkene and the C<sub>6</sub> to C<sub>12</sub> alkene is predominantly a C<sub>8</sub> alkene.

25. The process according to claim 24, wherein the C<sub>8</sub> alkene is a trimethylpentene.

26. A process for the hydrogenation of an alkene to an alkane, which process comprises contacting the alkene with a catalytic composite as claimed in any one of claims 14 to 16, and hydrogen, under catalytic distillation conditions.

27. The process according to claim 26 wherein the alkene is selected from trimethylpentene, n-octene, dimethylhexene and methylheptene.

28. The process according to claim 26 or 27, wherein the catalytic composite is admixed with inert distillation packing.

29. The process according to claim 28, wherein the ratio of the catalytic composite to inert distillation packing is from 10:1 to 1:10.

30. The process according to claim 28 wherein the catalytic composite and inert distillation packing are used in separate zones of the catalytic distillation column.

31. The process according to any one of claims 26 to 30, wherein the alkene is trimethylpentene and the alkane is trimethylpentane.

32. A process for preparing high octane compounds, the process comprising:

a) contacting a C<sub>2</sub> to C<sub>6</sub> alkene with a catalytic composite as claimed in any one of claims 1 to 16, under catalytic distillation conditions, to obtain a C<sub>6</sub> to C<sub>18</sub> alkene; and

5           b) contacting the C<sub>6</sub> to C<sub>18</sub> alkene from step a) with a catalytic composite as claimed in any one of claims 14 to 16, and hydrogen, under catalytic distillation conditions, to obtain a C<sub>6</sub> to C<sub>18</sub> alkane.

10       33.       The process according to claim 32, wherein the process steps a) and b) are carried out in a single catalytic distillation column.

34.       The process according to claim 32, wherein the process steps a) and b) are carried out in separate catalytic distillation columns.

15       35.       The process according to claim 32 or 33, wherein the C<sub>2</sub> to C<sub>6</sub> alkene is a C<sub>4</sub> alkene and the C<sub>6</sub> to C<sub>18</sub> alkene is a C<sub>8</sub> alkene.

36.       The process according to claim 35, wherein the C<sub>8</sub> alkene is trimethylpentene.

20       37.       A process for preparing high octane compounds, the process comprising:

a) contacting isobutene with a catalytic composite as claimed in any one of claims 1 to 16, under catalytic distillation conditions, to obtain trimethylpentene; and

25           b) contacting trimethylpentene with a hydrogenation catalyst, and hydrogen, under batch reaction conditions or under hydrogenation reaction conditions to obtain trimethylpentane.

38. A process for the production of C<sub>6</sub>-C<sub>18</sub> alkenes, which process comprises contacting a mixture of C<sub>2</sub>-C<sub>6</sub> alkenes with a catalytic composite as claimed in any one of claims 1 to 16, under catalytic distillation conditions.

5 39. A process according to claim 38, wherein each C<sub>2</sub>-C<sub>6</sub> alkene in the mixture is oligomerized within different reactive zones found in a single catalytic distillation column.

10 40. A process according to claim 38, wherein each C<sub>2</sub>-C<sub>6</sub> alkene is oligomerized within different reactive zones found in two or more linked catalytic distillation column.

41. A process according to any one of claims 38 to 40, wherein the mixture of C<sub>2</sub>-C<sub>6</sub> alkenes comprises one or more C<sub>4</sub> alkenes.

15 42. A process for the selective oligomerization of a lower alkene to a C<sub>6</sub>-C<sub>18</sub> alkene, which process comprises contacting a mixture of C<sub>2</sub> to C<sub>6</sub> alkenes and C<sub>1</sub> to C<sub>6</sub> alkanes with a catalytic composite as claimed in any one of claims 1 to 16, under catalytic distillation conditions.

20 43. A catalytic composite for use as a random packing hydrogenation catalyst in a catalytic distillation apparatus, the catalytic composite comprising:

25 a) a support structure, made of an inorganic oxide and having a void fraction ranging from 0.30 to 0.95, the support structure having a shape selected from a ring, a hollow cylinder, a cross or multi partition ring or cylinder with 2, 3, or 4 cell partitions, a saddle, a solid ring, a solid cylinder, a sphere, and a honeycomb body; and

b) from 0.01 to 10% by weight of palladium, platinum or rhodium, based on the weight of the catalytic composite, which is deposited on the support structure.

44. The catalytic composite according to claim 43,  
5 wherein the inorganic oxide is  $\alpha$ -alumina.

45. The catalytic composite according to claim 44,  
wherein the  $\alpha$ -alumina has a surface area of from 0.1 to 1.0  
m<sup>2</sup>/g.

46. A process for the hydrogenation of butadiene, the  
10 process comprising contacting butadiene with a catalytic  
composite as claimed in any one of claims 43 to 45, and  
hydrogen, under catalytic distillation conditions.

47. A process for the selective hydrogenation of  
methylacetylene and propadiene in a C3 fraction to provide  
15 propylene, the process comprising contacting the C3  
fraction with a catalytic composite as claimed in any one  
of claims 43 to 45, and hydrogen, under catalytic  
distillation conditions.

48. A process for the selective hydrogenation of  
20 allene and propyne in a fluid catalytic cracking (FCC)  
stream, the process comprising contacting the FCC stream  
with a catalytic composite as claimed in any one of claims  
43 to 45, and hydrogen, under catalytic distillation  
conditions.

49. A process for the selective hydrogenation of  
butadiene in a raffinate I or a raffinate II stream to  
provide a butene, the process comprising contacting the  
raffinate I or the raffinate II stream with a catalytic  
composite as claimed in any one of claims 43 to 45, and  
25 hydrogen, under catalytic distillation conditions.  
30